

REPORT DOCUMENTATION PAGE			Form Approved GMB No. 0704-0188
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1202, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>			
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	24 Jan 97	Final, 1 Oct 92 - 30 Sep 96	
4. TITLE AND SUBTITLE		5. FUNDING NUMBERS	
"Pseudo-Buckyballs" as Potential Superconductors		Grant Number F 49620-92-J-0523DEF 3484/RS 61103D	
6. AUTHOR(S)		7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	
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8. PERFORMING ORGANIZATION		AFOSR-TR- 05 97 0141	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. AGENCEY USE ONLY	
Air Force Office of Scientific Research Attn: Dr. Charles Lee Air Force Systems Command, USAF Bolling AFB, DC 20332-6448		PL	
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION/AVAILABILITY STATEMENT		12b. DISTRIBUTION CODE	
Public			
13. ABSTRACT (Maximum 200 words)			
<p>Alkali metal adducts to LOGEAs (Large Organic Globular Electron Acceptors) share with superconducting "Buckyball" adducts such as K₃C₆₀ the globular shape, delocalized π-systems and accessible reduction potentials that are believed important for superconductivity. This research focused on the synthesis and study of reduced macrobicyclic Schiff-base cryptands that have an aromatic linking group in each of the three strands. Some samples, when reduced with Rb or K, showed LFMA (Low Frequency Microwave Absorption) up to ~50 K and/or a pronounced diamagnetic downturn in the susceptibility below ~30 K. These phenomena are usually associated with superconductivity. The magnitude of these effects was, however, only that expected for traces (<1%) of superconducting phases and the effects were only present in a few samples. Much effort over a two-year time span was directed toward the identification and isolation of the phase(s) responsible, but without success. Although superconductivity could not be verified, these studies opened a new area of research; the study of the solid-state behavior of radical anion salts. Except for some crystal structure determinations, this field is virtually unexplored and is likely to lead to potentially useful electronic and magnetic materials. The stability at and above room temperature, even of multiply reduced compounds, is especially encouraging.</p>			
14. SUBJECT TERMS		15. NUMBER OF PAGES	
Fullerenes, LOGEAs, Superconductivity, Aromatic Anions, Alkali Metal Adducts, Cryptands, Schiff-bases		17	
16. PRICE CODE			
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
	Unclassified	Unclassified	

NSN 7540-01-280-5500

DTIC QUALITY INSPECTED

 Standard Form 298 (Rev. 2-89)
 Prescribed by ANSI Std. Z39-18
 298-102

Executive Summary

AFOSR Grant No. F49620-92-J-0523

“Pseudo-Buckyballs” as Potential Superconductors

James L. Dye, Principal Investigator

James E. Jackson, Co-Principal Investigator

David Tománek, Co-Principal Investigator

A. Publications that Acknowledge AFOSR Support

- 1) Tománek, D.; Zhong, W.; Krastev, E. *Phys. Rev. B* **1993**, *48*, 15461-15464.
- 2) Tománek, D.; Wang, Y.; Ruoff, R. S. *J. Phys. Chem. Solids* **1993**, *54*, 1679-1684.
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- 7) Wagner, M. J.; Dye, J. L.; Pérez-Cordero, E.; Buigas, R.; Echegoyen, L. *J. Am. Chem. Soc.* **1995**, *117*, 1318-1323.
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- 12) Craciun, L.; Jackson, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 12232-12233.
- 13) Stoudt, S.; Gopalan, P.; Bakulin, A.; Kahr, B.; Jackson, J. E. *Inorg. Chem.* **1996**, *35*, 6614-6621.

B. Other Publications Related to this Work

- 1) Stoudt, S. J.; Gopalan, P.; Kahr, B.; Jackson, J. E. *Struct. Chem.* **1994**, *5*, 335-340.
- 2) Jang, S.-H.; Mitchell, C.; Jackson, J. E.; Kahr, B. *Mol. Cryst. Liq. Cryst.* **1995**, *272*, 139-145.
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C. Papers in Preparation

- 1) De Backer, M. G.; Demol, F.; Sauvage, F. X.; Dye, J. L.; Ichimura, A. S.; Xie, Q., "A Spectroscopic Study of the Reduction of an Aromatic Schiff-base Cryptand in THF" 1996.
- 2) Szajek, L. P.; Huang, R. H.; Jackson, J. E., "Synthesis, Characterization, Fluxional Behavior of Polyaza Macrocyclic Cryptands with Chromophoric Linkages and their Cu¹ Cryptates" 1996.
- 3) Szajek, L. P.; Xie, Q.; Ichimura, A. S.; Wagner, M. J.; Huang, R. H.; Huang, S. Z.; Dye, J. L.; Jackson, J. E., "Naked Potassium Radical Anion Salts of 2,3-Bis(2-Pyridyl)Quinoxaline" 1996.

D. Abstracts of Meeting Presentations

D1. Posters

- 1) Szajek, L; Filonova, L.; Dye, J. L.; Jackson, J. E., "Alkali Metal Molecular Solids from Readily Prepared Globular Organic Substrates: A Route to Organic Superconductors", CFMR/Industry Symposium, Michigan State University, East Lansing, MI; Apr. 10-11, 1994.
- 2) Kaminski, A.; Rheault, M.; Peereboom, L; Jackson, J. E., "Triarylamine based Tripod Ethers and Aryloxides: Syntheses, Complexes, and Ion Binding", Great Lakes College Chemistry Conference, Michigan State University, East Lansing, MI; Apr. 9, 1994.
- 3) Jang, S.-H.; Mitchell, C.; Kahr, B.; Jackson, J. E., "Alkali Metal Ketyl Radicals: Systematics of High-Spin Coupling and Magnetic Susceptibility", Fourth International Conference on Molecule-Based Magnets, Salt Lake City, UT; Oct. 16-22, 1994.
- 4) Kahr, B.; Jang, S.-H.; Mitchell, C.; Misiolek, A.; Jackson, J. E., "Reevaluating Ion-induced High-Spin Associations of Spin-Labeled Crown Ethers", Fourth International Conference on Molecule-Based Magnets, Salt Lake City, UT; Oct. 16-22, 1994.
- 5) Misiolek, A.; Huang, R. Jackson, J. E., "Ferromagnetic Coupling By Alkali Metal Coordination: Structure And Magnetism In A Sodium Nitroxide Carboxylate", Spring 1995 ACS Meeting, Anaheim, CA.
- 6) Peereboom, L.; Ward, D. L.; Jackson, J. E., "Lanthanide Aratranes: Structures and Magnetism of 2,2',2"-Nitrilotriphenolate (=L) Complexes: Na₃L₂Gd(CH₃OH)₆(H₂O)₂; Na₃L₂Yb(CH₃OH)₅(H₂O)₂; L₂Gd₂(DMSO)₅; and L₂La₂(DMSO)₄", Spring 1995 ACS Meeting, Anaheim, CA.
- 7) Xie, Q.-S.; Szajek, L.; Wagner, M. J.; Dye, J. L.; Jackson, J. E., "Naked Potassium Radical Anion Salts of 2,3-Bis(2-Pyridyl)Quinoxaline", Spring 1995 ACS Meeting, Anaheim, CA.
- 8) Misiolek, A.; Huang, R.; Jackson, J. E., "Ferromagnetic Coupling By Alkali Metal Coordination: Structure and Magnetism of a Sodium Nitroxide Carboxylate", Spring CFMR Symposium, MSU; April 10, 1995.

- 9) Peereboom, L.; Ward, D. L.; Jackson, J. E., "Lanthanide Aratranes: Structures and Magnetism of 2,2',2"-Nitrilotriphenolate (=L) Complexes: $Na_3L_2Gd(CH_3OH)_6(H_2O)_2$; $Na_3L_2Yb(CH_3OH)_5(H_2O)_2$; $L_2Gd_2(DMSO)_5$; and $L_2La_2(DMSO)_4$ ", Spring CFMR Symposium, MSU; April 10, 1995.
- 10) Xie, Q.-S.; Szajek, L.; Wagner, M. J.; Dye, J. L.; Jackson, J. E., "Naked Potassium Radical Anion Salts of 2,3-Bis(2-Pyridyl)Quinoxaline", Spring CFMR Symposium, MSU, April 10, 1995.
- 11) Craciun, L.; Jackson, J. E., "Manxyl: An Unusually Persistent Simple Aliphatic Organic Radical", Gordon Conference on Free Radicals, Plymouth, NH; July 16-21, 1995.

D2. Talks

- 1) Fourth International Conference on Molecule-Based Magnets, Salt Lake City, UT; Oct. 16-22, 1994; "Metal Ion Complexes of the Free Radical Tris(2,6-dimethoxyphenyl)methyl and Related Nitroxyls"
- 2) Southeastern Magnetic Resonance Conference, University of North Carolina, Chapel Hill, NC; Oct. 23-25, 1994; "Toward a Biradical Ionophore: Ion Complexation by Tripod Ether Amines and Diamines".
- 3) Gordon Conference on Free Radical Reactions, Plymouth, NH; July 16-21, 1995; "Assembly of Organic Paramagnets by Ion Binding: A New Structural Approach to Molecular Magnetic Materials".
- 4) Fall ACS Meeting, Orlando, FL; Aug., 1996; "I-Manxyl: A Persistent Simple Alkyl Radical that Disproportionates via ϵ -Hydrogen Abstraction" (given by L. Craciun)

E. Personnel Supported in Part by This Grant (Includes Support from Matching MSU-CFMR Grant)

E1. Graduate Students (Note: Theses contain no or only partial descriptions of work under the AFOSR Grant - to appear in publications)

Name	Degree	Current Position
Kerry A. Reidy-Cedergren	Ph.D. (Chem.) 1996	Abbot Laboratories Chicago, Illinois
James E. Hendrickson	Ph.D. (Physics) 1994	Asst. Prof., Univ. of Wisconsin, Eau Claire
Michael J. Wagner	Ph.D. (Chem.) 1994	Asst. Prof., George Washington University

Name (Cont.)	Degree (Cont.)	Current Position (Cont.)
Songzhan Huang	Ph.D. (Chem.) 1994	Degree Candidate (Chem. Engineering)
Liliana Craciun	Current Ph.D.	Candidate (Chemistry)
Tibor Nagy	Current Ph.D.	Candidate (Physics)
Scott Stoudt	Ph.D. (Chem.) 1995	Postdoc, (Chemistry)
Andrzej Misiolek	Current Ph.D.	Candidate (Chemistry)
Sei-Hum Jang	Ph.D. (Chem.) 1993	Dae Woo Institute for Advanced Engr., Korea
Kevin Conley	Current Ph.D.	Candidate (Physics)
Lars Peereboom	Current M.S.	Candidate (Chemistry)
Hong-In Lee	Ph.D. (Chem.) 1994	Postdoc, Northwestern Univ. Evanston, IL

E2. *Postdoctoral Research Associates and Visiting Faculty* (Note: Some of these researchers worked only on short, specific problems relevant to the CFMR Grant)

Rosario Concepcion	Visiting Faculty	Pontificia Universidad Catolica, Santiago, Dominican Republic
Marc De Backer	Visiting Faculty	HEI - CNRS Lille, France
James Waner	Summer High School Visiting Faculty	High School Chemistry Teacher
Lawrence Szajek	Postdoc	NIH, Silver Springs, MD
Lubov Filonova	Postdoc	Postdoc, Univ. of California, Santa Cruz, CA
Qingshan Xie	Postdoc	Current
Andrew Ichimura	Postdoc	Current
Deborah Gilbert	Postdoc	Rayovac Corporation Madison, WI

Technical Summary

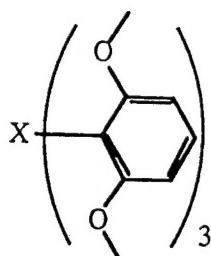
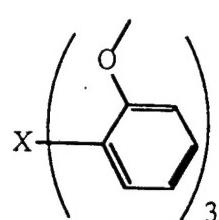
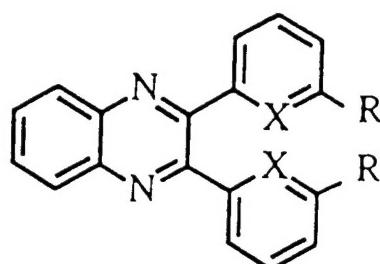
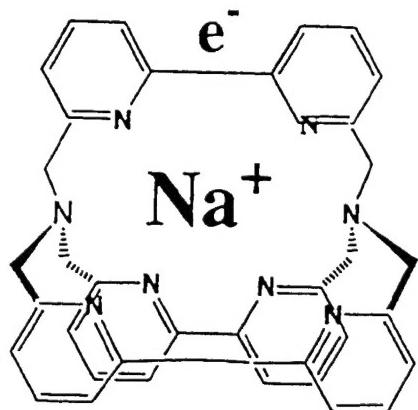
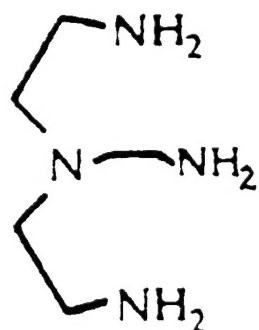
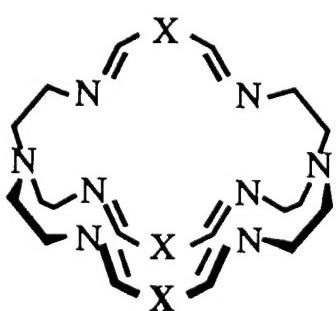
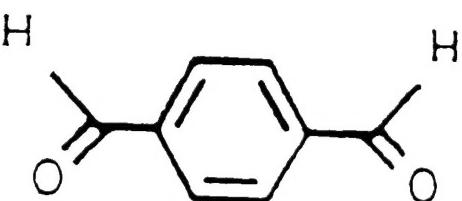
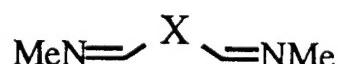
Synthesis

The working hypothesis in attempts to synthesize a new class of superconductors was based upon the formation of anions of LOGEAs (Large Organic Globular Electron Acceptors) by their reaction with alkali metals. By analogy to reactions of alkali metals with fullerenes to form superconducting compounds such as K₃C₆₀, it was thought that large aromatic molecules capable of accepting more than one electron would be attractive candidates.

To establish the techniques needed to study more complex compounds, initial experiments were carried out with tripod ethers¹, **1** and **2**, reduced with sodium. Another model system was quinoxaline, **3**, reduced with potassium.² A reduced LOGEA that had been previously studied by Echegoyen, Lehn and co-workers^{3,4} was sodium cryptatium, **4**, but its synthesis is complex. It led, however, to a joint study⁵ with Echegoyen of Ru(bipyridyl)₃ and to a search for more easily synthesized aromatic cryptands. Based upon methods described in the literature,⁶⁻⁸ a class of Schiff-base cryptands was chosen for study. These are readily synthesized on a gram-scale by the reaction of the triamine **5** with an aromatic di-aldehyde such as **6**. A large number of Schiff-base cryptands with the general formula **7** were synthesized as indicated in Figure 1, along with the single-strand reference compounds, **8**.

The Schiff-base cryptands provide ideal LOGEAs for study. They are readily synthesized, easily reduced, can accept up to three electrons per molecule, and form thermally stable anions upon reaction with alkali metals. A major problem, however, has been the inability to grow suitable crystals of the anion salts for X-ray diffraction studies. In the one crystal structure that has been obtained, that of **7a**·K·2(CH₃NH₂), the K⁺ ion is, surprisingly *outside* of the complexant and is strongly coordinated by methylamine. Many attempts were made to crystallize other adducts, particularly those which utilize lithium as a reductant, since it is likely that Li⁺ is encapsulated within the cryptand cavity. No suitable crystals were obtained, although as described below, a number of studies were made with powdered samples, frozen solutions and liquid solutions of the reduced Schiff-base cryptands.

Structural Formulas

**1****2****3**
 $X = N, R = H$ **4**
Cryptatium**5**
Reactants for Schiff-base Cryptand Synthesis**7**
 $X = \text{Aromatic}$ **8**
 $X = \text{Aromatic}$

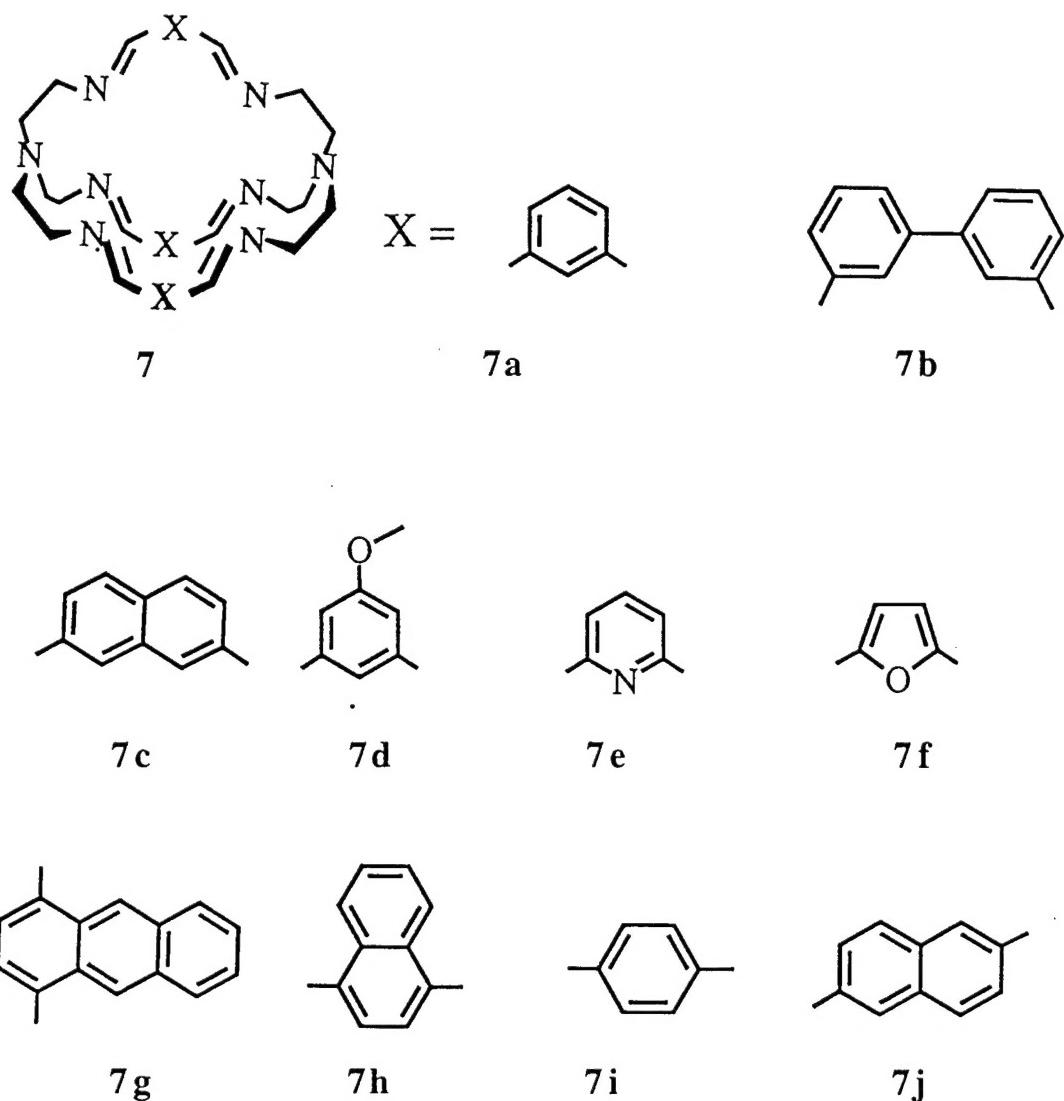


Figure 1. Aromatic Schiff-base cryptands that have been synthesized in our laboratory.

Indications of Superconductivity (SC)

The most obvious sign of SC, zero resistance, is not usually found in early studies because only a small fraction of the sample is superconducting. Identification of the phase responsible and its purification are required to yield a sample that has zero resistance and magnetic flux exclusion (Meissner effect). There are two general methods in addition to resistivity that are used to identify the presence of a SC phase in an impure sample. The most sensitive of these is LFMA (Low Field Microwave Absorption) also called MMA (Magnetosensitive Microwave Absorption) in which an EPR signal centered at zero field is observed that decreases as the temperature is increased and

disappears at the critical temperature.⁹⁻¹⁴ This effect reflects the limited penetration of eddy currents into a superconducting particle and has been described as a definitive indicator of SC when the characteristic temperature dependence is observed.¹⁵

The second indicator of SC is a pronounced onset of diamagnetism as the temperature is reduced below T_c. Since a pure superconductor has a (volume) susceptibility of - 1/4p, less than 1% of a superconductor in a sample would have an easily detectable downturn in the magnetic susceptibility.

The present research was carried out in collaboration with a former student, Dr. Marc De Backer, a Professor in the HEI (Haute Etude Industrielle) in Lille, France and a member of the CNRS. When he reported¹⁶ the observation of LFMA in samples of the Schiff-base cryptand **7a** reduced with K or Rb (see Figure 2), an intensive two-year search began in both his laboratory and ours, to investigate the source of this effect. Dr. De Backer spent time in our laboratory to further study these systems.

Not all samples showed LFMA, but some samples in both laboratories gave positive results and two preparations also showed a marked downturn in the magnetic susceptibility starting at ~ 30 K (Figure 2). The magnitude of the latter effect, if due to SC, indicated the presence of only about 0.05% SC phase. This effect on the susceptibility was never observed with subsequent samples.

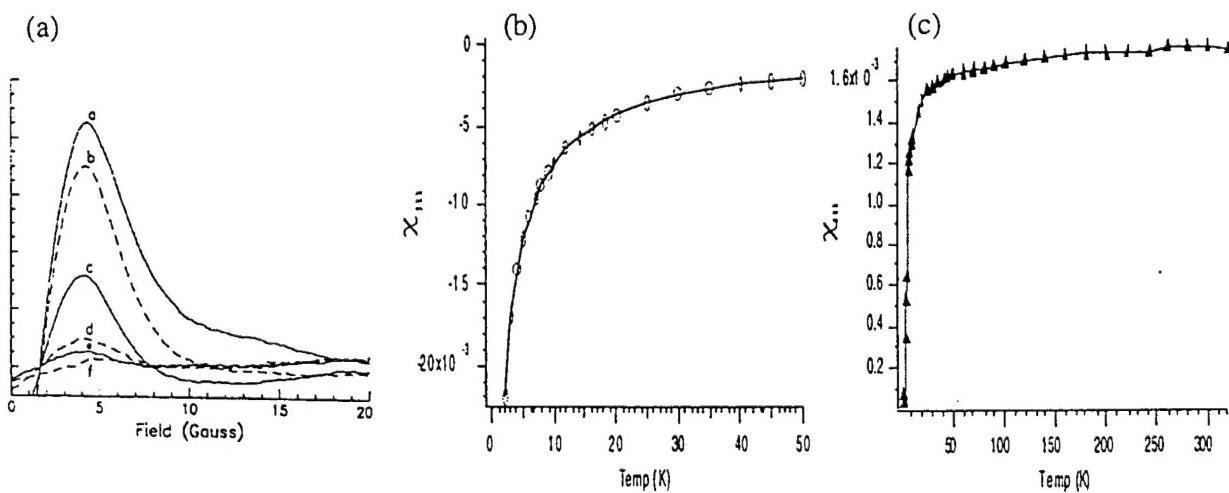


Figure 2. (a) LFMA of Rb + **7a** at T up to 50 K¹⁶. (b) and (c) Molar Magnetic Susceptibilityy of Rb + **7a** and K + **7b**, respectively.

It has gradually become apparent that the presence of LFMA is a necessary, but not sufficient condition for superconductivity. It was observed in an organic ferromagnet¹⁷ and Veinger, Zabrodskii and Tisnek¹⁵ found LFMA signals in some oxide glasses doped with transition metals and reported its observation by others in gallium arsenide grown at low temperatures (which they attributed in all cases to the presence of superconducting phases). After our inability to isolate the phase(s) responsible and even the observation of weak LFMA signals in some of the empty EPR sample tubes, we concluded that LFMA can arise from other causes than superconductivity. The downturn in magnetic susceptibility is harder to dismiss, but it was not observed with subsequent samples, so it may have been due to instrumental artifacts. Indeed, a recent report from the De Backer lab¹⁸ showed that even an empty Suprasil tube can give a downturn in the susceptibility!

Properties of Reduced Schiff-Base Cryptands

Optical Spectra:

Although attempts to isolate a superconducting phase from reduced Schiff-base cryptands occupied an inordinate amount of time, these compounds continue to be good candidates for the study of optical, electronic and magnetic properties. Studies of the optical absorption spectra of solutions in tetrahydrofuran (THF), methylamine (MeNH_2) and dimethyl ether (Me_2O) of a number of reduced aromatic compounds and of thin solvent-free films of the same compounds generally show similar results.¹⁹ The films are formed by vapor co-deposition of the alkali metal and complexant onto a sapphire substrate in high-vacuum, by deposition of the alkali metal on a solvent-evaporated film of the complexant, or by evaporation of solvent from a “wet” film of solution on an optical window within a quartz cell. The solution spectrum of the Schiff-base cryptand **7a** in tetrahydrofuran (THF) as a function of time of exposure to a K film is shown in Figure 3. Formation of the mono-anion results in a peak at 620 nm and a broad peak at ~ 1350 nm (Fig 3, solid line). Further reduction to the dianion results in disappearance of these two peaks and formation of a peak at ~ 460 nm (Fig. 3, dashed bottom line). This behavior has

been verified by studies with stoichiometric amounts of K and **7a**. There is evidence that contact ion-pair formation may also play a role since the IR peak is strongly solvent-dependent and also changes when a complexant for K^+ is added. We do not yet fully understand the origin of these effects but they imply that on the optical time scale the electronic charge may be localized on a strand or strands near the counter-cation.

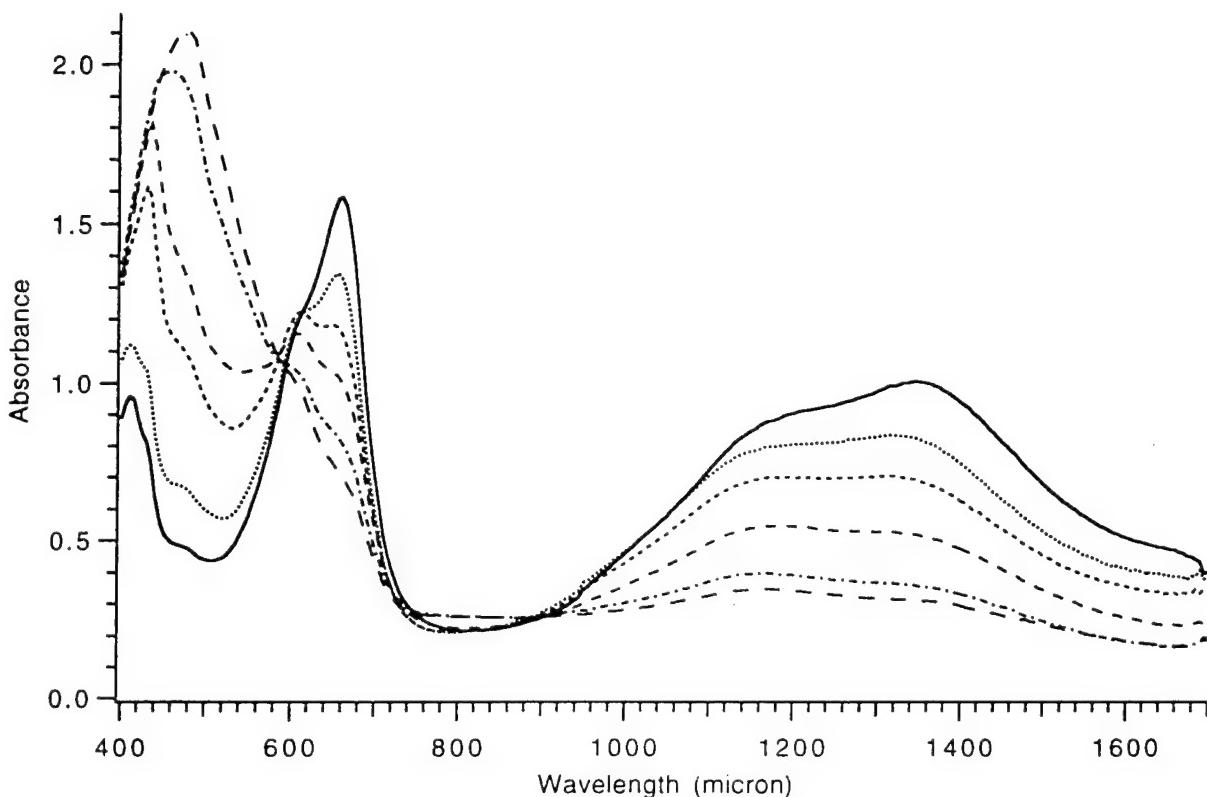


Figure 3. Variation of the optical spectrum of K metal + **7a** in THF at -40 °C with time of standing over a metal film. The spectrum given by the solid line is that of the mono-anion radical. Changes with time correspond to the formation of the dianion, whose spectrum is given by the final (dashed) line.

Cyclic Voltammetry:

C-V studies in THF are difficult because of the low solubility of supporting electrolytes. It was necessary to carry them out at room temperature. This has the disadvantage that THF tends to react with the reduced species. Figure 4 shows the presence of two reversible reduction waves of **7a** as well as a third irreversible reduction wave. These results agree with the ease of synthesis of the dianion. With the naphthalene Schiff-base cryptand **7c**, the trianion salt is readily formed with

rubidium. Thus a large family of mono-, di- and tri-anions of a variety of Schiff-base cryptands is available for study.

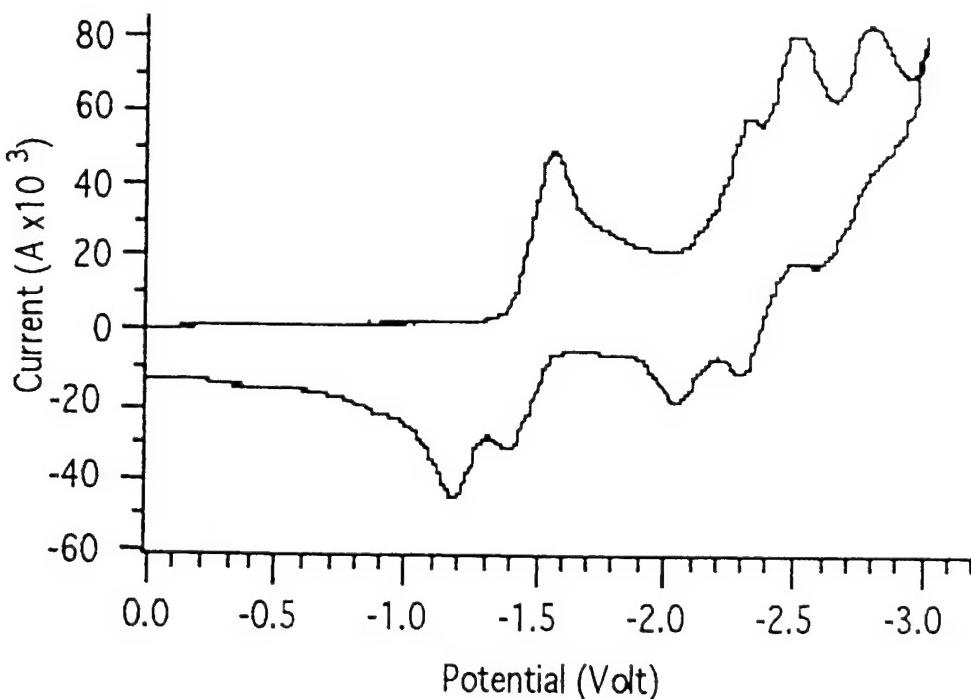


Figure 4. Cyclic voltammogram of **K + 7a** in THF at room temperature showing two reversible reduction waves and one irreversible reduction wave. The reference compound (0 volts) is ferrocene.

EPR Spectra:

Extensive EPR studies of various reduced Schiff-base cryptands in solution in THF, Me_2O , MeNH_2 and benzene have been made, and anions of the single strand reference compound, **8** have also been studied. Hyperfine coupling to nitrogens and hydrogens are observed for the contact ion-pair with the mono-anion of **7a**.¹⁹ On the EPR time scale, all three strands are equivalent, showing that the cation can move around the molecule without dissociation. Addition of a cryptand complexant for the cation removes the hyperfine coupling and shows that rapid ion-pair dissociation and association can occur for solvent (-or complexant-) separated ion pairs.

Figure 5 gives some representative examples.

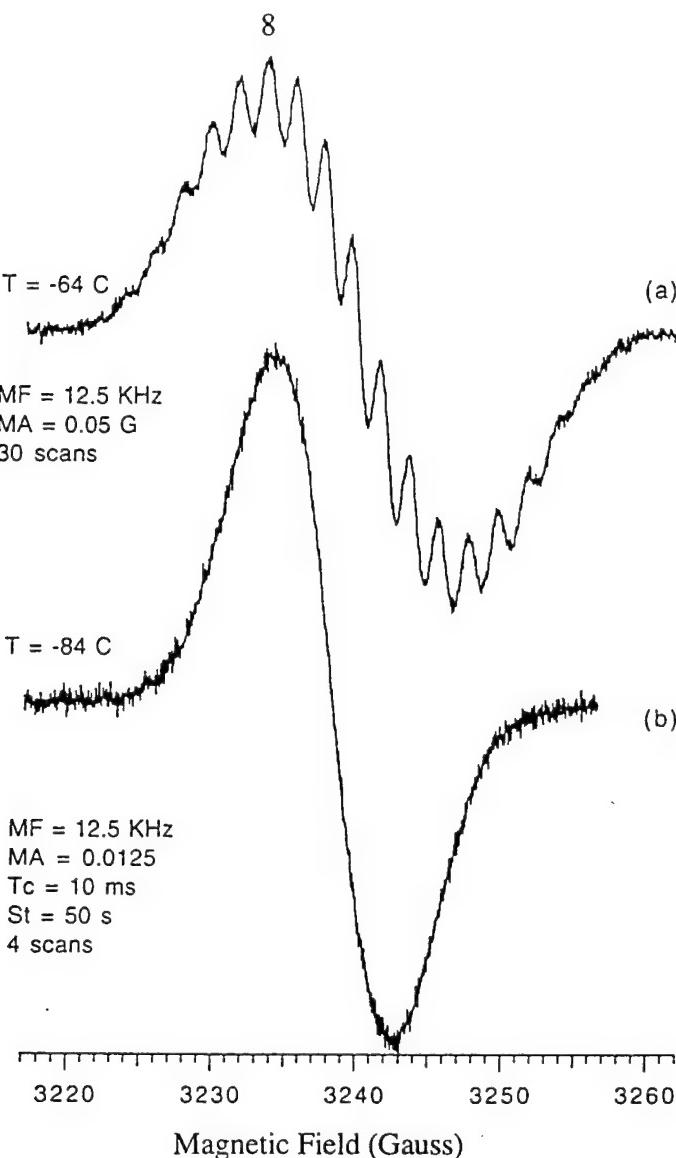


Figure 5. EPR spectra of **K + 7a** in dimethyl ether without (a) and with (b) the addition of cryptand [2.2.2]. Spectrum (a) is that of the contact ion-pair between K and the mono-radical anion, while that of (b) is from the complex-separated ion-pair.

The EPR spectra of dianions show very strong absorptions, which suggests that a singlet state is *not* formed, but rather that the di-reduced molecule is similar to a bi-radical. The tri-anion of **7c** with Rb forms a quintet state.

Magnetic Susceptibility:

Except for the two anomalous samples described above, the magnetic susceptibilities of powdered samples of the mono-anion salts of **7a, b, c** are as expected for a paramagnetic system. The susceptibilities obey the Curie-Weiss law with relatively weak antiferromagnetic interactions.

Some show a maximum in the susceptibility. We have not yet studied the magnetic susceptibilities of di- and tri-anion salts.

Thermal Stabilities:

Although THF solutions of the reduced Schiff-base cryptands are unstable, the solid powders and solutions of them in benzene and toluene are thermally stable at room temperatures and above (up to ~ 80°C). This portends well for future applications if the solid salts have useful optical, electronic or magnetic properties. The inability to prepare solvent-free crystals has impeded studies of the solid-state properties, but we feel that the study of solid compounds of alkali metals and LOGEAs , an area of research that is virtually unexplored, is certainly worth pursuing in the future.

Theory and Modeling

The initial thrust of theoretical calculations was to use tight-binding calculations to determine the electronic energy levels of LOGEAs, for correlation with optical spectra, reduction potentials and magnetic coupling. This was then to be extended to permit calculation of electron-phonon coupling as a prelude to the interactions that might lead to superconductivity. Our inability to obtain the structures of solvent-free alkali metal adducts to LOGEAs made such calculations difficult, since it was first necessary to use molecular modeling to estimate structures. As a result, the theoretical efforts focused on two related areas as described below.

Fullerene Structures and Properties:

The Tománek research group carried out a number of calculations of fullerene stability, structure and vibrational spectra. This resulted in nine publications that acknowledged AFOSR support (see the Executive Summary). These calculations were particularly important in characterizing multi-shell carbon fullerenes and nanotubes.

Modeling Void Spaces in Crystal Structures:

Of importance to electron-electron interactions in electrides and in communication between anions of LOGEAs is the nature of the void spaces in crystals. Another area where such visualization is important is the geometry of the inter-molecular spaces in zeolites and similar porous crystalline systems. With support from the AFOSR Grant, programs were developed that permit easy visualization of the void spaces when the crystal structure is known. The method also permits examination of anion and cation trapping sites in such crystals. For example, the shapes and connectivities of the interstitial sites in alkali metal reduced C₆₀ are readily studied with these methods.

The development and application of these programs was described in a paper that acknowledged AFOSR support.²⁰ The programs and instructions for their use are available without charge by anonymous FTP from argus.cem.msu.edu with the directory path /pub/dye/voids.

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- (1) Stoudt, S. J.; Gopalan, P.; Kahr, B.; Jackson, J. E. *Inorg. Chem.* **1996**, *35*, 6614-6621.
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